

Mechanism of direct oxidation of cyclohexene to cyclohexanone with nitrous oxide. Theoretical analysis by DFT method

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New very effective results on the liquid-phase oxidation of cyclohexene to cyclohexanone by nitrous oxide are analyzed using the B3LYP/6-31G* approximation to predict a two-step reaction mechanism correlated with the experimental data.

In the last decade nitrous oxide (N₂O) has attracted growing attention as a selective oxygen donor for oxidation reactions in the gas phase.^{1–4} Recently, Panov *et al.*^{5,6} described also the liquid-phase oxidation of alkenes by N₂O with nearly 100% selectivity. This approach has been exemplified by the oxidation of cyclohexene to cyclohexanone⁵ and cyclopentene to cyclopentanone.⁶ The lack of a need to use catalysts and solvents coupled with very high selectivity makes these reactions very promising for practical applications. However, their reaction mechanism is not clear and its theoretical investigation may be rather useful.

This work is the first attempt to elucidate the total mechanistic route of cyclohexene oxidation using the experimental data.⁵ The authors^{5,7} postulated the oxidation of double bond C=C to proceed *via* the intermediate formation of 1,2,3-oxadiazoline. The 1,3-dipolar cycloaddition was analyzed in a number of theoretical studies.⁸ The DFT calculations of cycloaddition of 16-electron 1,3-dipoles with ethylene showed that these reactions are exothermic.⁸ Note that the subsequent rearrangement and N₂ cleavage were not discussed in the above works.

In the present study we analyze the paths of cyclohexene oxidation to cyclohexanone by nitrous oxide *via* N₂O cycloaddition to cyclohexene or formation of cyclohexene epoxide intermediate. To provide further conversion of cyclohexene epoxide to cyclohexanone, high activation energy should be

overcome. At the same time we have found a direct route of 1,2,3-oxadiazoline transformation to cyclohexanone with a reasonable value of activation energy $E^* = 22$ kcal mol⁻¹.

The calculations were carried out using the GAUSSIAN98 program package⁹ within the Density Functional Theory approach¹⁰ with the Becke three-parameter exchange functional within the gradient corrections,^{11,12} and the Lee-Yang-Parr correlation functional¹³ with the 6-31G* basis set¹⁴ (B3LYP/6-31G* approximation). For the identification of transition states (TS) we have used the QST2 method with the subsequent calculation of frequency's normal modes and intrinsic reaction coordinate (IRC). This approximation, as numerous calculations of similar systems show,¹⁵ provides a good description of energy parameters (reaction heats, reaction routes, and activation energies), equilibrium geometry structures, and vibration frequencies. As was found in the calculations of 1,3-dipolar cycloaddition of N₂O to an ethylene molecule,⁸ this approach gives results which are close to those of the considerably more expensive CCSD(T) level.

The calculations predict a two-step mechanism of the reaction. Fig. 1 shows the energy profile of the steps and basic structural parameters of the stable intermediates and reaction product. Actually, the cycloaddition reaction of 1,3-dipolar to cyclohexene with nitrous oxide^{8,16} is the first step. The direct interaction between cyclohexene and N₂O (reactants R) results in the opening of double bond C=C and formation of intermediate dihydro-1:2:3-oxadiazoline (INT1), which includes heterocycle C–N=N–O–C with bonds N–N = 1.23 Å and N–O = 1.43 Å. These bond lengths essentially differ from those of the N₂O molecule: N–N = 1.14 Å and N–O = 1.19 Å. Note that stability of intermediate INT1 with respect to reagents ($\Delta H_1 = -7.7$ kcal mol⁻¹) is probably sufficient for experi-

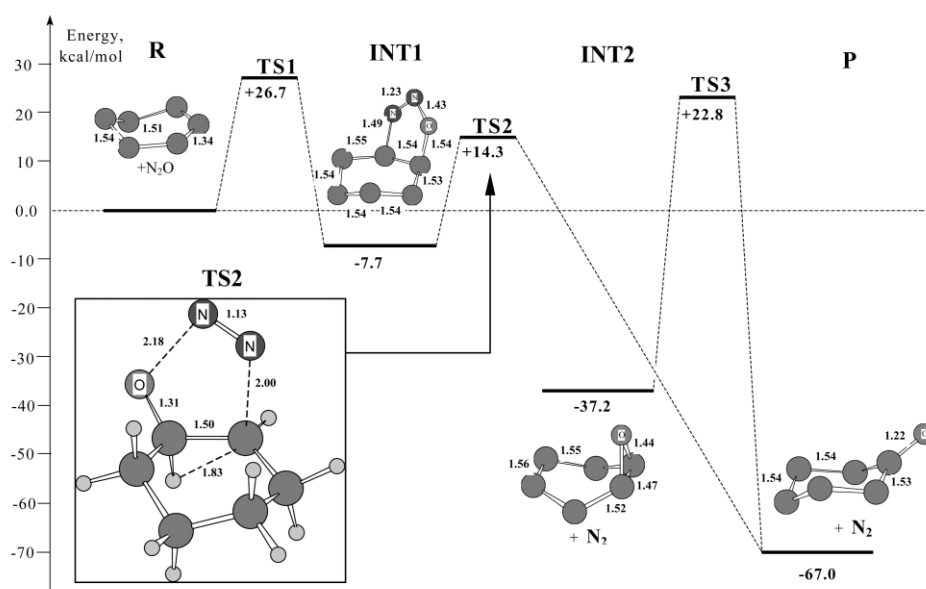


Fig. 1 Profile of energy surface R → TS1 → INT1 → TS2 → P (R → cyclohexene + N₂O, P → cyclohexanone + N₂) for the two-step mechanism of direct oxidation of cyclohexene to cyclohexanone with nitrous oxide. Relative energies are measured from reactants.

mental detection at low temperatures. The carbon framework is in *trans*-configuration. The transition from reactants R to INT1 is an activated process, $R \rightarrow TS1 \rightarrow INT1$. This reaction route probably involves formation of a precursor complex preceding transition state TS1, as shown elsewhere.⁸ Since the stability of this complex is *ca.* 1 kcal mol⁻¹, activation energy of this step is determined in general by the energy of transition state TS1 ($E^* = 27$ kcal mol⁻¹). The calculations of vibration frequencies of TS1 and IRC show that this TS1 actually binds initial reagents R and INT1, its single imaginary frequency is $\nu(TS1) = 452i$ cm⁻¹.

The process of INT1 formation was studied by scanning bond length $r = C-O$. For $r > 3.0$ Å, an N₂O molecule is linear and normal to the carbon cycle. The molecule parameters are close to those in the gas phase, and angle CON is equal to 180°. When N₂O approaches to cyclohexene, starting with $r < 3.0$ Å, CON reduces to 90° and angle NNO decreases to 135° at a time. For $C-O = 2.17$ Å, the system reaches transition state TS1, the structure of the five-membered heterocycle is similar to that of heterocycle INT1 (the structure is shown in Fig. 1), and its parameters are as follows: N-N = 1.18 Å, N-O = 1.24 Å, C-N = 2.01 Å, C-O = 2.17 Å, C-C = 1.40 Å. Note that close parameters were obtained by Su *et al.*⁸ for the cycloaddition reaction of ethylene to N₂O. It is possible to guess that the first step of oxidation of both aliphatic and cyclic olefins proceeds through transition states of a similar structure.

The second step involves the subsequent decomposition of INT1, formation of the target product (P), cyclohexanone, due to transition of hydrogen within the carbon cycle: OC1H1-C2H → O=C1-C2H₂. The process is also activated: INT1 → TS2 → P. For C2-H1 = 1.83 Å, the system reaches transition state TS2 (the TS2 parameters are shown in Fig. 1). This hydrogen shift is responsible for significant changes in the structure of both carbon ring and the five-membered heterocycle. In this case, the carbon bound with oxygen changes its hybridization sp³ → sp², providing a shift of electron density to π-bond O=C, cleavage of the N-O bond in the heterocycle (N-O = 2.18 Å for TS2), removal of a nitrogen molecule into the gas phase (C-N = 2.00 Å and N-N = 1.13 Å for TS2). For the second step, the calculated parameters are: $\nu(TS2) = 437i$ cm⁻¹, and $E^* = 22$ kcal mol⁻¹.

Bridson-Jones *et al.*⁷ suggested that cyclohexene epoxide might be an intermediate of the reaction of olefin oxidation by N₂O. We have studied this reaction route. The calculations suggest two stable *cis*- and *trans*-isomers of cyclohexene epoxide. The stability of the *cis*-isomer is higher than that of *trans*-isomer by 2.5 kcal mol⁻¹. If one assumes that the *cis*-isomer is an intermediate INT2 (see Fig. 1), then transition INT2 → P proceeds through transition state TS3. The calculated parameters are: $\nu(TS3) = 690i$ cm⁻¹, and $E^* = 60$ kcal mol⁻¹. The analysis of IRC shows that TS3 binds INT2 and P. The overall reaction $R \rightarrow TS1 \rightarrow INT1 \rightarrow TS2$; $INT2 \rightarrow TS3 \rightarrow P$ (see Fig. 1) is -67 kcal mol⁻¹ exothermic.

The first step of the reaction can be considered as the activation of a nitrous oxide molecule, providing the N₂O decomposition and creation of active oxygen through formation of an adduct with cyclohexene (INT1). As Fig. 1 suggests, bonds N-N = 1.23 Å and N-O = 1.43 Å are significantly weakened compared to the initial molecule. Electron density is rearranged so that oxygen gets electrophilic properties, which promotes an opening of double bond C=C and formation of two new bonds: C-O = 1.45 Å and C-N = 1.49 Å. We believe this is a limiting step that determines the activation energy of the overall reaction. Panov *et al.* have shown that $E^* = 21$ kcal mol⁻¹ for the oxidation reaction of cyclopentene to cyclopentanone.⁶ It should be noted that the reaction proceeds under milder conditions compared to the oxidation of cyclohexene, for which one should expect a higher activation energy. According to our estimation, $E^* = 27$ kcal mol⁻¹. It is important that INT1 is a

weakly bound intermediate ($\Delta H_1 = -7.7$ kcal mol⁻¹), which predetermines a low value of the activation energy of the next step.

The second step governs the nature of the desired product. We have considered only two probable products, cyclohexanone and cyclohexene oxide. At catalytic liquid-phase oxidation of alkenes with N₂O, the reaction channel with formation of epoxides is possible.^{17,18} In the case of non-catalytic oxidation, this channel is eliminated. Actually, our calculations have shown that there is no reaction channel connecting INT1 and cyclohexene epoxide (INT2), and so, if cyclohexene epoxide forms under the given reaction conditions, it transforms into cyclohexanone, $INT2 \rightarrow TS3 \rightarrow P$. It was shown above that the barrier height for TS3 is high enough (*ca.* 60 kcal mol⁻¹), which excludes this reaction route. This result agrees with the conclusion by Panov *et al.*⁵ that cyclohexene oxide introduced into the reaction mixture is not involved in the chemical transformation. Thus, cyclohexanone is the only product of oxidation of cyclohexene with nitrous oxide.

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